Pérez-Dorado, A., F. Piérola, I., Baselga, J., Gargallo, L. & Radic, D. (1989). Complexation of poly(monobenzyl itaconate) and poly(N-vinyl-2-pyrrolidone) in dilute solution. *Die Makromolekulare Chemie*, 190 (11), pp. 2975-2981.

DOI: 10.1002/macp.1989.021901128

Complexation of poly(monobenzyl itaconate) and poly(N-vinyl-2-pyrrolidone) in dilute solution

*Angel Perez-Dorado, Ines R Pierola**

Departamento de Química Física I, Fac. de Ciencias, UNED, Senda de! Rey s/n, 28040 Madrid, Spain

Juan Baselga

Departamento de Materiales y Producci6n Aeroespacial, ETSI Aeronáuticos, Universidad Politécnica, 28040 Madrid, Spain

Ligia Gargallo, Deodato Radic

Fac. de Química, Pontificia Universidad Cat6lica de Chile, Casilla 6177, Santiago, Chile

SUMMARY:

Upon mixing dilute solutions (10^{-4} - 10^{-2} mol/l) of poly(monobenzyl itaconate) (PMBI) and poly(N-vinyl-2-pyrrolidone) (PVP) in methanol, soluble polycomplex particles are formed. Here we report on the spectrophotometric determination of the turbidity of different solutions of PVP and PMBI as a function of polymer concentration and PVP molecular weight. Viscosity measurements were also performed. The polycomplex is weak. Polycomplex particles are more compact and much larger than separated chains of polyacid and polybase. No definite stoichiometry is observed and a microgel-like structure is proposed.

Introduction

The cooperative interaction of two complementary polymers gives place to the formation of polycomplexes [1] (PCs). They have recently found several important applica-tions: They are used for casting ultrafiltration membranes [2], in template polymeriza-tions [3] or in the design of polymeric materials to be used in interfaces [4]. The forma-tion of PCs in aqueous solution represents a simple model for some biological processes [4, 5]; but the most promising application of PCs is probably to enhance polymer miscibility [6-9].

PCs are stabilized through different types of intractions [1], but we will be concerned only with hydrogen-bonded PCs. In that group of PCs, the system poly(acrylic acid)/ poly(ethylene oxide) has been broadly studied (ref. [10-15] and refs. therein). Some other PCs, formed by carboxylic [1, 4-7, 16, 17] or sulfonic [2, 8, 18] polyacids with PVP [16, 17] poly(vinylpyridines) [1, 2, 4, 6, 8, 18, 19], or some other polybases [7, 20, 21], have also been studied.

The object of this work is to study the interaction of poly(monobenzyl itaconate) (PMBI) and poly(*N*-vinyl-2-pyrrolidone) (PVP) in methanol solution. It is known [16] that poly(monomethyl itaconate) does not form a PC with poly(ethylene oxide), but it reacts in equimolar stoichiometry with PVP in aqueous solution. In our system there

are no hydrophobic interactions, so that the extrapolation of results in solution to polymer blends in bulk could be better achieved.

Experimental part

Materials

Four samples of poly(*N*-vinyl-2-pyrrolidone) (PVP, from Aldrich Co.) were used: PVP10, PVP24, PVP40 and PVP36. Their weight-average molecular weights, given by the supplier, are 10000, 24000, 40000, and 360000, respectively.

Poly(monobenzyl itaconate)*) (PMBI) was synthesized by radical polymerization[22] and fractionated. One fraction was chosen for this work. It is atactic[23] (*mm* = 0,26, *mr* = 0,48, *rr* = 0,26), and its molecular weight, viscometrically determined, is $3{,}8 \cdot 10^4$.

Methanol (MeOH) of RS quality (special for fluorimetry) was purchased from Carlo Erba.

Measurements

Turbidimetric measurements were performed on a Shimadzu UV 240 spectrophotometer. Temperature in the sample holder was controlled by means of a thermocirculating bath Lauda RM-6.

Viscosities were determined with a Lauda Viscotimer automatic viscometer at 25,0 ± 0,05 °C. The kinetic energy correction was applied. Densities were measured with an Anton Paar DMA 55 digital densimeter at the same temperature as viscosities.

Polymer solutions were obtained by mixing MeOH and MeOH solutions of PMBI and PVP in different proportions. The order of addition was always the same: PMBI solution, MeOH and finally PVP solution. The reason is that we have found some influence of the processing variables on the formation of the PC[24], but results were reproducible once that those variables were controlled. After preparing the samples, they were shaken vigorously and left for some minutes before performing any measurement on them.

Results and discussion

The absorption spectra of PMBI in MeOH dilute solution ($2 \cdot 10^{-3}$ mol/l) extend from 300 nm to lower wavelengths and shows a plain line in the range 400–600 nm (Fig. 1). The same holds for PVP in the visible region (Fig. 1). Upon mixing those PMBI and PVP solutions, the base line of the absorption spectra is very much curved (Fig. 1), because light scattering of the mixture is much larger than for the separated polyacid and polybase solutions. The turbidity of the mixtures remains constant for all the time we have observed them (several months); it is also thermally stable in the range 10–50 °C and increases with polymer concentration. At polymer concentrations about 10^{-1} mol/l, phase separation takes place at room temperature (r. t.).

Those results reveal the formation of a PC which is soluble in MeOH at r. t. (if polymer concentrations are low enough) and whose particles are much larger than the mixed macromolecules. In order to characterize it, we have determined spectrophotometrically the turbidity (τ) of some PC solutions.

*) Systematic name: 3-Benzyloxycarbonyl-2-methylenepropionic acid.

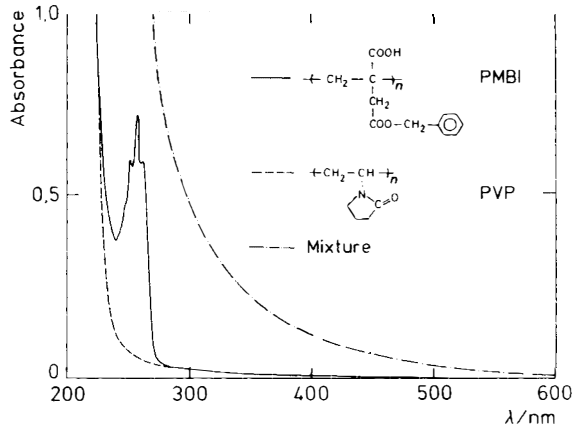

Fig. 1. UV spectra of solutions in methanol of PMBI ($5{,}0 \cdot 10^{-3}$ mol/l), PVP ($5{,}0 \cdot 10^{-3}$ mol/l) and their 1 : 1 mixture

Turbidimetric measurements

The Mie theory yields the next expression[25] for the turbidity of an optically heterogeneous system with spherical and isotropic particles suspended in a continuum medium,

$$\tau(\lambda) = \frac{3c \int_0^\infty D^3 Q(a, n) f(D)\, dD}{2d \int_0^\infty D^3 f(D)\, dD} \tag{1}$$

where c represents the concentration of scattering particles in g/cm^3, d is their segmental density, a is a function of the ratio of the particle diameter (D) and the wavelength (λ) of the incident light, ($a = \pi D/\lambda$), n is the particle-to-solvent refractive index ratio, $Q(a, n)$ represents the absorption efficiency, and $f(D)$ the distribution function of particle sizes. The τ experimentally observed can be due *a priori* to absorption and scattering of light. To consider only the scattering contribution, the imaginary part of the particle and solvent refractive index must be neglected. In such case, assuming that $D \ll \lambda$, and that there is not multiple scattering (dilute solution), $Q(a, n)$ can be expanded[26] in a power series of D:

$$\tau(\lambda) = \frac{3c}{2d\,\bar{D}_3} \sum_i \Gamma_i \bar{D}_{i+2} \tag{2}$$

where $\bar{D}_i$ represents the i-th moment of the particle size distribution. In the absence of absorption, the coefficients of the fifth order[27] approximation are zero except the fourth one; Eq. (2) becomes then,

$$\tau(\lambda) = \frac{4c\pi^4}{d} \left[\frac{n^2 - 1}{n^2 + 2}\right]^2 \frac{\bar{D}_6\, n_1^4}{\bar{D}_3\, \lambda_0^4} = \frac{S}{\lambda_0^4} \tag{3}$$

where n_1 is the solvent refractive index and λ_0 the wavelength of the incident light in vacuum. Eq. (3) simplifies to

$$S = \frac{24\pi^3 Vc}{d}\left[\frac{n^2 - 1}{n^2 + 2}\right]^2 n_1^4 \tag{4}$$

where V is the weight-average volume of the scattering particles.

In spite of its simplicity, the Mie theory has been found useful in explaining the influence of molecular size on the absorption spectra of macromolecules[28].

Fig. 2 type plots are linear in any case, and, therefore, S represents a measurement of the solution turbidity independent of the wavelength. The PC refractive index can

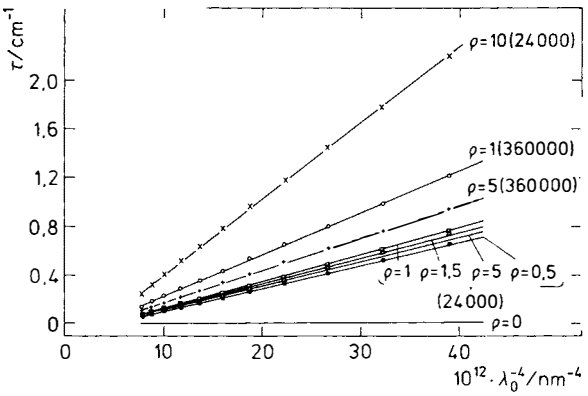

Fig. 2. Plot of tubridity τ versus λ_0^{-4} for several solutions with different polybase-to-polyacid ratio ρ and PVP molecular weight (in brackets). [PMBI] = $6{,}3 \cdot 10^{-3}$ mol/l in any case; ρ = [PVP]/[PMBI]

be considered constant and equal to the average of PMBI[29] (1,58) and PVP[30] (1,53) refractive indexes, i.e. n = 1,17.

According to Eqs. (3) and (4), S is proportional to the PC concentration and volume and depends inversely on its segmental density. Lets consider separately each one of those quantities.

Polycomplex strength

Let us assume that the PC is formed in an equilibrium reaction of f monomeric units of PVP per one monomeric unit of PMBI. If the equilibrium constant (K) is very large (strong PC), the PC concentration is proportional to the first power of the concentration of the reactant in defect. Keeping constant the polyacid concentration, and increasing ρ, the ratio of polybase-to-polyacid amount concentrations, the concentration of a stong PC increases linearly at low ρ values and levels off abruptly when $\rho = f$, where f is the stoichiometric factor. That is a behaviour found for several PCs[1,10].

On the other hand, if K is very small (weak PC), the PC concentration is proportional to both the polyacid and polybase concentrations. For $\rho = 1$, S should depend on $[PMBI]^{\nu}$ with $\nu = 2$. Fig. 3 shows that S depends parabolically on [PMBI] ($\rho = 1$) and does not depend appreciably on the PVP molecular weight. Double logarithmic plots of S versus [PMBI] confirm that ν is about 2 (Tab. 1), and hence, we can conclude that the PC studied is weak.

The formation of a PC is a cooperative process. There exists a certain range of polyacid and polybase chain lengths outside which the cooperative binding is not

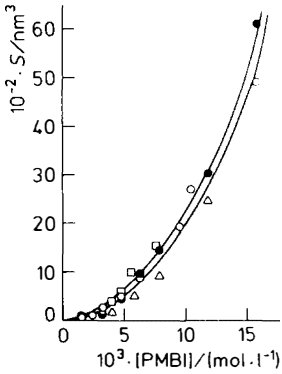

Fig. 3.

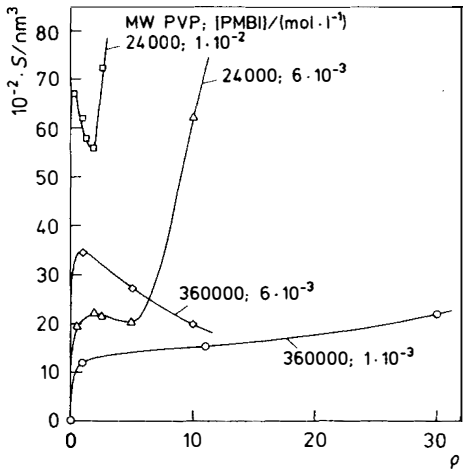

Fig. 4

Fig. 3. Plot of S (cf. Eq. (4)) versus [PMBI] at polybase-to-polyacid ratio $\rho = 1$ for different PVP molecular weights; (○): PVP10, (●): PVP24, (△): PVP40, (□): PVP360

Fig. 4. Plot of S (cf. Eq. (4)) versus polybase-to-polyacid ratio ρ for different [PMBI] and PVP molecular weights, as indicated in the figure

possible[10]. That range depends on the polymer structure and on solvent. In the PC studied here, the polybase minimum chain length is below 90 monomeric units (PVP10) and the cooperative interaction takes place in a broad range of polybase molecular weights ($1 \cdot 10^4$ to $3{,}6 \cdot 10^5$). A similar result was found[10] for the system poly-(monomethyl itaconate)/PVP in methanol, but in *N,N*-dimethylformamide, PCs are formed with PVP molecular weights up to $5 \cdot 10^4$.

Polycomplex stoichiometry

Fig. 4 shows the dependence of S on ρ for several PVP molecular weights and PMBI concentrations. If the stoichiometric factor f would not depend on ρ, S should increase

with ρ without maxima or minima. According to Fig. 4 this is not the case, and therefore f cannot be ascribed to a definite value. At the monomeric level, the polyacid-polybase interaction is 1 : 1, but bound sequences are joined by unbound parts that interact with solvent, and this makes the PC soluble. The proportion of single polymer loops with respect to PC sequences depends on ρ and PVP molecular weight. It is, therefore, a microgel-like structure, and the particles' volume must be expected to depend on ρ and chain length.

Tab. 1. Values of ν from the double logarithmic plot of S vs. $[PMBI]^{\nu}$, as a function of the PVP molecular weight

ν	$\bar{M}_w$ (PVP)
1,98	10 000
1,97	24 000
1,98	40 000
2,24	360 000

Tab. 2. Gain of viscosity g as a function of [PMBI] for polybase-to-polyacid ratio ρ = 1 and PVP360

g	$\frac{10^3 \cdot [PMBI]}{mol \cdot l^{-1}}$
0,25	1,0
0,51	2,0
0,74	3,0
0,68	5,0
0,64	7,5
0,63	10,0

Polycomplex segmental density

It is usually considered that the formation of a PC can be observed viscometrically if the hydrodynamic volume of the complex is different (generally smaller) from the sum of hydrodynamic volumes of polyacid and polybase. This comparison is made through the concept of gain in viscosity, g:

$$g = (\eta_{sp})_{PC}/[(\eta_{sp})_{PA} + (\eta_{sp})_{PB}] \quad (5)$$

where η_{sp} represents the specific viscosity of the PC, the polyacid (PA) and the polybase (PB), at the corresponding concentrations. Fig. 5 shows the dependence of g on ρ, and Tab. 2 summarizes g values as a function of PMBI concentration with ρ = 1. g is less than 1 in any case, and therefore the PC is very compact. The PC compactness does not depend much on [PMBI] except for very low concentrations. It shows a minimum for ρ between 1 and 2. At larger ρ values, g increases, and it may even

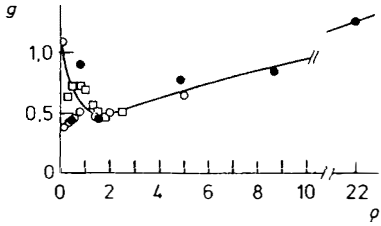

Fig. 5. Gain of viscosity g as a function of polybase-to-polyacid ratio ρ for several conditions; (●): [PMBI] = $3{,}9 \cdot 10^{-3}$ mol/l, PVP360; (○): [PMBI] = $1{,}0 \cdot 10^{-3}$ mol/l, PVP24; (□): [PMBI] = $1{,}01 \cdot 10^{-2}$ mol/l, PVP24

become larger than 1, indicating that the microgel particles are highly branched in those conditions.

In consequence, the PC segmental density changes with ρ and v cannot be considered constant with that variable. This is in accordance with the results of turbidimetry. It can be concluded that each polyacid chain joins to several chains of polybase, and the effective ratio of monomeric units of each type, the volume and the structure of the final PC particle depend on the polybase-to-polyacid ratio much more than on the polymer concentrations.

Financial support from *CICYT* under grant no. GG85-0013 is gratefully acknowledged. We also wish to acknowledge the assistence of Dr. *I. Hernandez-Fuentes* in the viscosity measurements.

[1] I. F. Pierola, M. Caceres, P. Caceres, M. A. Castellanos, J. Nuñez, *Eur. Polym. J.* **24**, 895 (1988)
[2] J. Desbrieres, M. Rianudo, *Eur. Polym. J.* **17**, 1265 (1981)
[3] J. Smid, Y. Y. Tan, G. Challa, *Eur. Polym. J.* **19**, 853 (1983)
[4] V. A. Izumrudov, A. P. Savitskii, K. N. Bakeev, A. B. Zezin, V. A. Kabanov, *Makromol. Chem., Rapid Commun.* **5**, 709 (1984)
[5] P. L. Dubin, J. M. Murrell, *Macromolecules* **21**, 2291 (1988)
[6] J. Y. Lee, P. C. Painter, M. M. Coleman, *Macromolecules* **21**, 954 (1988)
[7] J. Y. Lee, P. C. Painter, M. M. Coleman, *Macromolecules* **21**, 346 (1988)
[8] A. Natansohn, E. Eisenberg, *Macromolecules* **20**, 323 (1987)
[9] J. M. Rodriguez-Prada, V. Percec, *Macromolecules* **19**, 55 (1986)
[10] E. A. Bekturov, L. A. Bimendina, *Adv. Polym. Sci.* **45**, 99 (1981)
[11] E. Tsuchida, K. Abe, *Adv. Polym. Sci.* **45**, 1 (1982)
[12] B. Bednar, Z. Li, Y. Huang, L. Ch. P. Chang, H. Morawetz, *Macromolecules* **18**, 1829 (1985)
[13] H. T. Oyama, W. T. Tang, C. W. Frank, *Macromolecules* **20**, 1839 (1987)
[14] (a) I. Illiopoulos, R. Audebert, *Polym. Bull. (Berlin)* **13**, 171 (1985); (b) I. Illiopoulos, R. Audebert, C. Quivoron in *"Reversible Polymer Gels and Related Systems"*, ed. by P. S. Russo, ACS Symp. Ser. 1987
[15] E. Kokufuta, A. Yokota, I. Nakamura, *Polymer* **24**, 1031 (1983)
[16] L. A. Bimendina, E. A. Bekturov, G. S. Tleubaeva, V. A. Frolova, *J. Polym. Sci., Polym. Symp.* **66**, 9 (1979)
[17] H. Ohno, K. Abe, E. Tsuchida, *Makromol. Chem.* **179**, 755 (1978)
[18] A. S. Michaels, R. G. Miekka, *J. Phys. Chem.* **1**, 765 (1961)
[19] D. J. Skrovanek, M. M. Coleman, *Polym. Eng. Sci.* **27**, 857 (1987)
[20] M. M. Coleman, D. J. Skrovanek, J. Hu, P. C. Painter, *Macromolecules* **21**, 59 (1988)
[21] P. C. Painter, Y. Park, M. M. Coleman, *Macromolecules* **21**, 66 (1988)
[22] M. Yazdani-Pedran, L. Gargallo, D. Radic, *Eur. Polym. J.* **21**, 707 (1985)
[23] A. Horta, I. Hernandez-Fuentes, L. Gargallo, D. Radic, *Makromol. Chem., Rapid Commun.* **8**, 523 (1987)
[24] A. Perez-Dorado, J. Baselga, D. Radic, L. Gargallo, I. F. Pierola, to be published
[25] M. Kerker, *"The Scattering of Light and Other Electromagnetic Radiations"*, Academic Press, New York 1969
[26] L. H. Garcia-Rubio, *ACS Symp. Ser.* **332**, 161 (1987)
[27] R. B. Penndorf, *J. Opt. Soc. Am.* **52**, 896 (1962)
[28] L. H. Garcia-Rubio, *Macromolecules* **20**, 3070 (1987)
[29] I. Hernandez-Fuentes, private comunication
[30] *"Polymer Handbook"*, ed. by J. Brandrup, E. H. Immergut, 2nd ed., Wiley, New York 1975